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Article

Value-Added Products from Urea Glycerolysis Using a Heterogeneous Biosolids-Based Catalyst

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Abstract: Although thermal hydrolysis of digested biosolids is an extremely promising strategy for wastewater management, the process economics are prohibitive. Here, a biosolids-based material generated through thermal hydrolysis was used as a catalyst for urea glycerolysis performed under several conditions. The catalytic system showed remarkable activity, reaching conversion values of up to $70.8 \pm 0.9\%$ after six hours, at $140\text{ }^{\circ}\text{C}$ using a catalyst/glycerol weight ratio of 9% and an air stream to remove NH_3 formed during the process. Temperature played the most substantial role among reaction parameters; increasing temperature from $100\text{ }^{\circ}\text{C}$ to $140\text{ }^{\circ}\text{C}$ improved conversion by 35% and glycidol selectivity by 22%. Furthermore, the catalyst retained good activity even after the fourth catalytic run (conversion rate of $56.4 \pm 1.3\%$) with only a slight decrease in glycidol selectivity. Thus, the use of a biosolids-based catalyst may facilitate conversion of various glycerol sources (i.e., byproduct streams from biodiesel production) into value-added products such as glycidol, and may also improve the economic feasibility of using thermal hydrolysis for treatment of biosolids.

Keywords: biosolids; urea glycerolysis; glycidol; glycerol carbonate; catalyst

1. Introduction

Over the last twenty years, the increased accountability of companies with regards to environmental issues has represented a formidable driving force for the development of sustainable industrial processes [1,2]. As a consequence, the production of fuels and chemicals has started to use recycled or renewable feedstocks in place of oil-based raw materials [3,4] in an attempt to improve process sustainability while maintaining performance of traditional commodities. Nowadays, biodiesel is one of the most well-established technologies based on renewable resources [5], and its production has been increasing every year, partly because of government environmental policies [6]. The increase in biodiesel production has made available abundant amounts of glycerol, a byproduct stream that can be used as feedstock for several chemical syntheses [7]. Among them, the production of glycerol carbonate is of key interest, as it could be used for the synthesis of high-performance hyperbranched polymers [8,9].

Glycerol carbonate is typically produced in a two-step process from the carboxylation of ethane or propene oxide and a subsequent reaction with glycerol [10]. A one-step synthesis of glycerol carbonate has also been reported by several authors through reaction of glycerol with supercritical CO_2 [11], or using urea [12,13] or other reagents [14]. Urea glycerolysis is an economically attractive procedure because of the low cost of the reagents and higher yields compared with other routes [15]. In addition, during urea glycerolysis, glycerol carbonate can undergo decarboxylation with the formation of glycidol, a highly reactive compound that could potentially replace glycerol carbonate in the production of polymers, leading to higher quality materials [9]. Despite the better performance of glycidol in

polymer applications, its synthesis is particularly hazardous and environmentally unfriendly as it involves hydrolysis and dehydrochlorination of epichlorohydrin [16].

To improve classical synthetic pathways, several authors have reported new catalytic systems for the selective conversion of glycerol to glycerol carbonate [17,18]. However, the synthesis of glycidol has remained challenging and catalytic systems generally lead to the formation of both glycerol carbonate and glycidol [12,17,19,20]. Radical decarboxylation of glycerol carbonate is an interesting alternative procedure that could be combined with the urea glycerolysis process because urea undergoes radical heterolytic cleavage at temperatures higher than 130 °C [21] forming highly reactive species that lead to the degradation of cyclic carbonates [22]. Several catalytic systems were proposed to enhance the urea reactivity during alcoholysis [23], but metal oxides are typically employed because of their low cost, high recyclability, and good catalytic performances [24,25].

For this purpose, a very attractive source of metal salts and metal oxides is represented by biosolids, a byproduct generated during the treatment of municipal wastewater. Several authors reported the use of biosolids and sewage sludge as iron-based catalysts [26,27]. Furthermore, biosolids ashes were used in several catalytic conversions such as switchgrass gasification [28], pyrolysis of industrial wastes [29], and for organic pollutants removal [30].

Recently, our group reported that thermal hydrolysis of biosolids dramatically increased natural settling rates [31]. Although thermal hydrolysis offers an intriguing solution for treatment and disposal of biosolids, the capital and operating costs may be prohibitive to mainstream adoption. Here, we report that the solid residue remaining after thermal hydrolysis of biosolids, which contains a high concentration of metals, particularly metal oxides (i.e., Fe_2O_3 , Al_2O_3 , ZnO , TiO_2 and silica), acts as a catalyst for conversion of glycerol to value-added products. Finding value for this solid residue may improve the process economics for the thermal hydrolysis of biosolids, making it a more attractive solution for wastewater treatment facilities. In this work, the metal-rich solid residue recovered after thermal hydrolysis of biosolids was successfully used as heterogeneous catalyst for urea glycerolysis. For these experiments, several parameters were investigated: Temperature, time, catalyst loading, urea/glycerol molar ratio, and residual atmosphere. Based on our findings, the solid residue obtained after thermal hydrolysis of biosolids has great potential for enhancing urea glycerolysis.

2. Results and Discussion

2.1. Assessment of the Biosolids-Based Catalyst

Urea glycerolysis can proceed through two different mechanisms, a radical or a non-radical pathway (Figure 1). The first step of both pathways involves the formation of a urethane intermediate. This compound evolves through an intermolecular esterification into glycerol carbonate. Subsequently, glycerol carbonate could undergo decarboxylation, which results in the formation of glycidol.

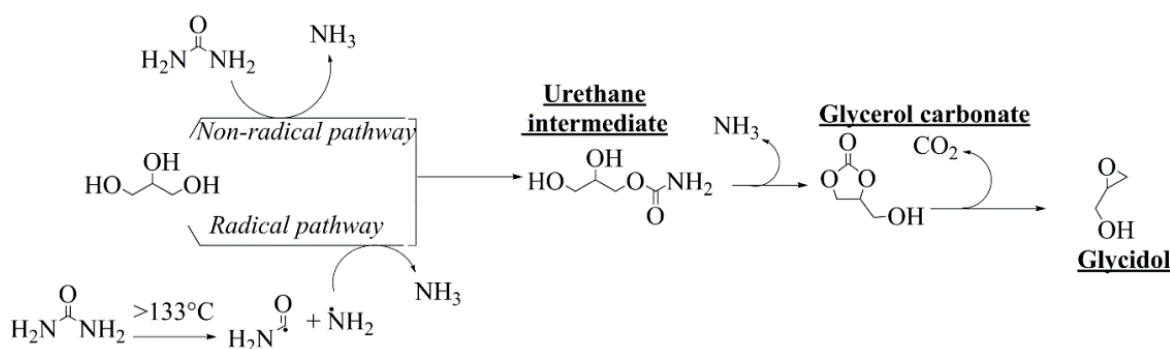


Figure 1. Radical and non-radical reaction pathways for formation of glycerol carbonate and glycidol during urea glycerolysis.

It has been shown that urea glycerolysis could be performed under catalytic conditions using several metal-based materials containing Zn, Al, Fe, Ti, and other metals [32]. The biosolids-based material used as catalyst in these experiments is a dark brown fine powder (Figure 2) and contains an inorganic fraction (30.3 ± 0.6 wt %) that comprises several metal species (Table 1), mainly as oxides, and silica [31].



Figure 2. Biosolids-based catalyst as recovered from hydrolysis of biosolid at 280 °C for 1 h.

Table 1. Concentration of the main metal species in biosolids-based catalysts as determined by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

	Concentration of Main Metal Species [mg/g]								
	Cr	Fe	Mn	Sr	Al	Cu	Zn	Pb	Ti
Biosolids-based catalyst ¹	0.39 ± 0.02	26 ± 1	0.58 ± 0.03	0.37 ± 0.02	26 ± 1	0.71 ± 0.04	1.06 ± 0.05	0.10 ± 0.01	3.2 ± 0.2
Recycled biosolids-based catalyst ²	0.28 ± 0.01	18 ± 1	0.39 ± 0.5	0.28 ± 0.01	20 ± 1	0.74 ± 0.03	0.72 ± 0.05	0.08 ± 0.01	0.16 ± 0.02

¹ The native biosolids-based catalyst obtained through thermal hydrolysis of biosolids; ² A recycled biosolids-based catalyst that had been used for four urea glycerolysis reactions.

As reported by Climent et al. [12], the direct interactions between urea, glycerol, and the surface of metal oxides can promote the alcoholysis process. Thus, a heterogeneous catalyst containing a mix of aluminum and zinc oxides, such as the biosolids-based material used in these experiments, has great potential in the production of glycerol carbonate and glycidol. In addition, the biosolids-based catalysts showed a remarkable concentration of surface acidic sites (5.32 ± 0.03 mmol/g) that could enhance the decarboxylation of carbonates [33,34]. Finally, as shown by the FT-IR spectrum (Figure 3), carboxylic bands ($\nu_{\text{OH}} = 3400\text{--}3300$ cm^{−1}, $\nu_{\text{C=O}} = 1800\text{--}1700$ cm^{−1}) are weaker compared with ν_{CH} (2900–2800 cm^{−1}) and $\nu_{\text{C=C}}$ (1680–1600 cm^{−1}), supporting the hypothesis that acid sites are mainly inorganic rather than carboxylic functionalities.

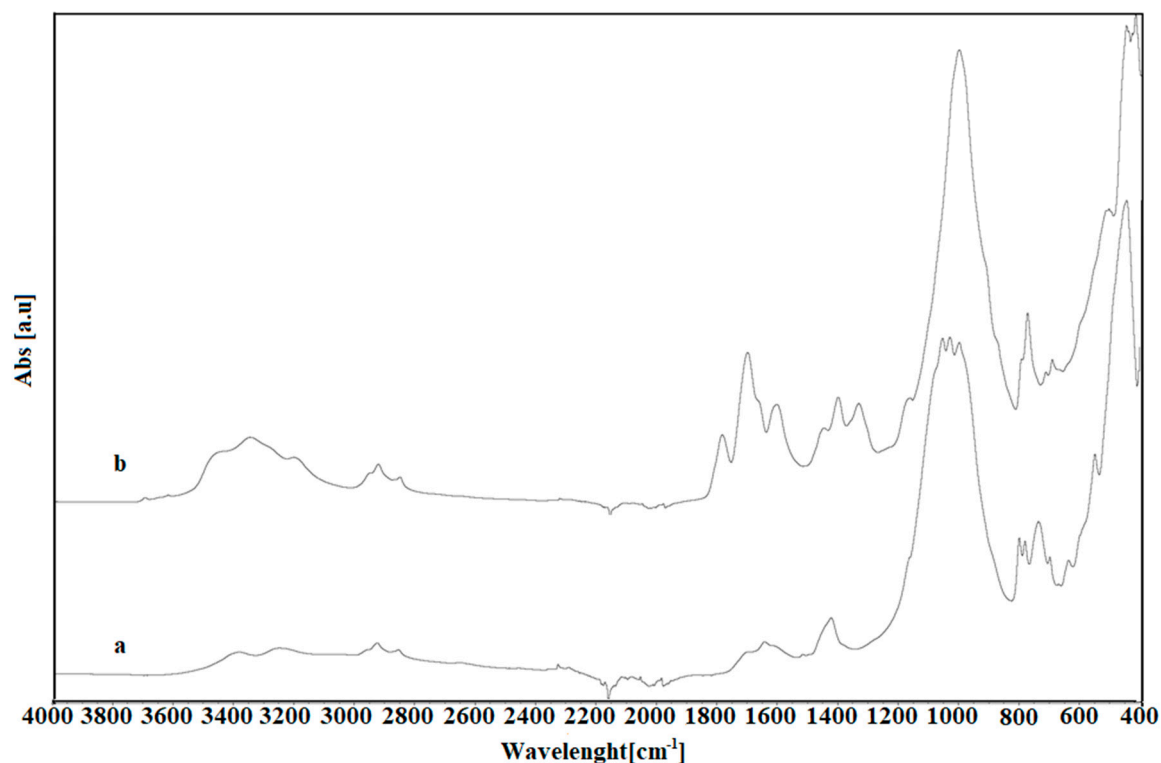


Figure 3. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The spectrum generated in the range of 4000 to 400 cm^{-1} is shown for the native biosolids-based catalyst (a) and a recycled catalyst that had been used in four catalytic reactions (b).

2.2. Influence of Catalyst Loading

The influence of catalyst loading on conversion and selectivity of urea glycerolysis was studied at 140 °C with a 2:1 molar ratio of urea:glycerol and an air stream to remove NH_3 formed during the reaction (Figure 4). The conversion rates achieved with the non-catalytic system were lower than those obtained using any combination of reaction time and catalyst loading, with a maximum conversion value of $46.8 \pm 0.6\%$ reached after 6 h. Increasing the catalyst loading from 0 to 3 wt % improved the conversion and after 6 h, a value of $64.1 \pm 0.4\%$ was achieved. Further improvements in conversion were observed for catalyst loading of 6 wt % ($66.5 \pm 0.4\%$ after 6 h) and for 9 wt % ($69.4 \pm 0.9\%$ after 6 h), but with a catalyst loading of 12 wt % the conversion values were not significantly different ($p < 0.05$) from those achieved using 9 wt %. The glycidol selectivity for the non-catalytic system was quite high (up to $83.4 \pm 0.6\%$ after 6 h), meanwhile the highest value achieved using the catalytic system was $70.8 \pm 0.4\%$ after 6 h using 12 wt % of catalyst loading.

As reported by Aresta et al. [11], the formation of glycerol carbonate is slower than the decarboxylation process, so in the non-catalytic system at 140 °C, carbonates were degraded to glycidol due to the radical-rich environment granted by the heterolytic splitting of urea. Conversely, the catalytic system increased the reaction rate between reactive species formed by radical degradation of urea and glycerol leading to an increase in conversion and an increase in decarboxylation. Thus, considering the glycidol yields (calculated as the conversion multiplied by selectivity), the catalytic system outperformed the non-catalytic one with maximum glycidol yields of $49.7 \pm 0.9\%$ (after 6 h using 9 wt % of catalyst) and $39.0 \pm 1.0\%$ (after 6 h without catalyst), respectively. Based on analysis of variance (ANOVA) outputs, parameters investigated (reaction time and catalyst loading) were statistically significant for both conversion and selectivity values during urea glycerolysis ($p < 0.05$).

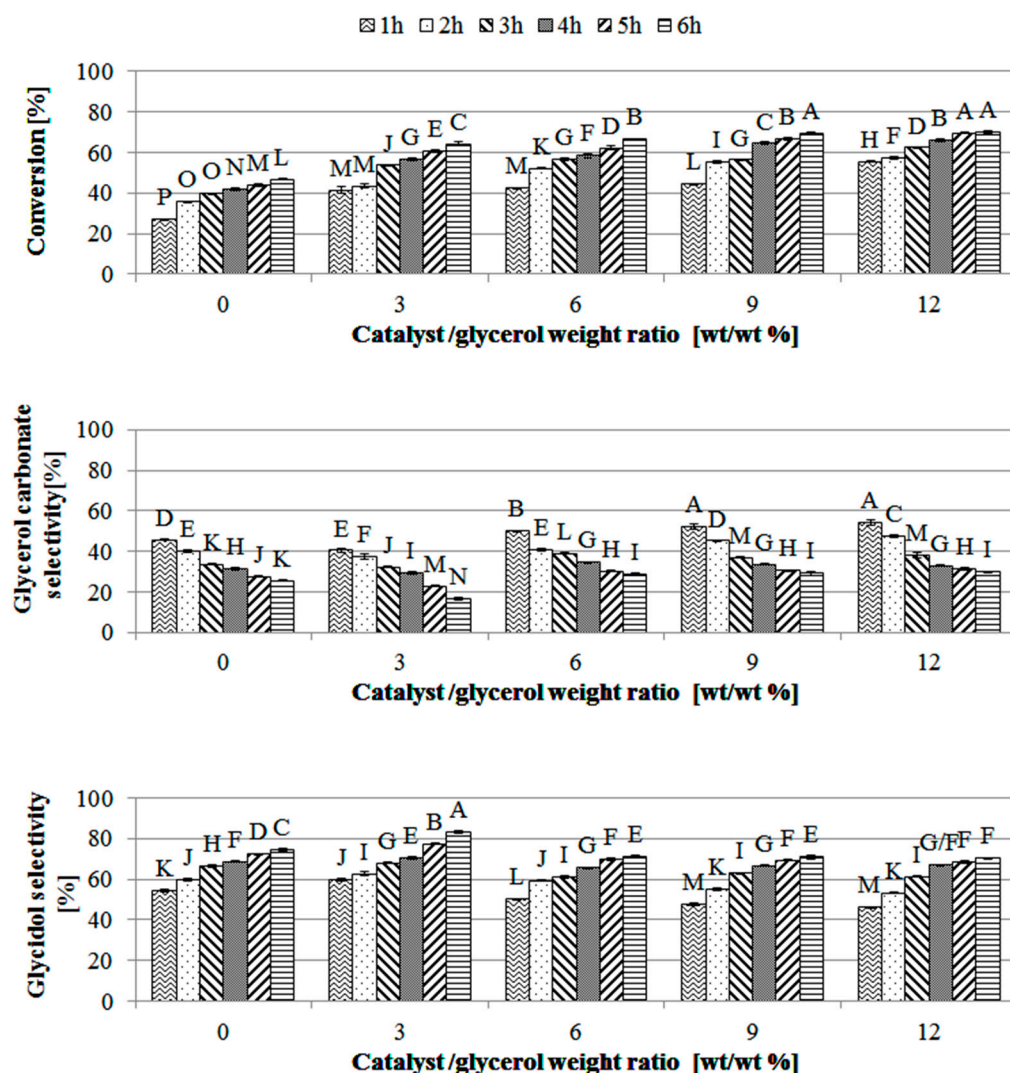


Figure 4. The influence of catalyst loading on the catalytic performance of a biosolids-based catalyst. Reactions were performed at 140 °C, with a 2:1 molar ratio of urea:glycerol, and the use of an air stream to promote the forward reaction. For these experiments, different catalyst:glycerol loading ratios (0 wt %, 3 wt %, 6 wt %, 9 wt %, 12 wt %) were examined. The means of triplicate experiments are reported, with the error bars representing standard deviations. Data annotated with different letters are significantly different (confidence level of 95%).

2.3. Influence of Temperature

Temperature is a key parameter for every catalytic conversion and was shown to have a dramatic effect on urea glycerolysis (Figure 5). At 100 °C, the maximum conversion achieved after 6 h was $44.2 \pm 0.2\%$, with a drastic decrease to $13.6 \pm 0.9\%$ for the 1 h reaction. Increasing the temperature to 120 °C improved the conversion rate after 1 h and 2 h, but the conversion values for the remaining reactions (3 h to 6 h) were not significantly different ($p < 0.05$) from those achieved at 100 °C at a given reaction time. A further increase of temperature up to 140 °C drastically improved the conversion of the reaction. After only 1 h at 140 °C, the conversion achieved ($44.3 \pm 0.2\%$) equaled those obtained at 100 °C and 120 °C after 6 h.

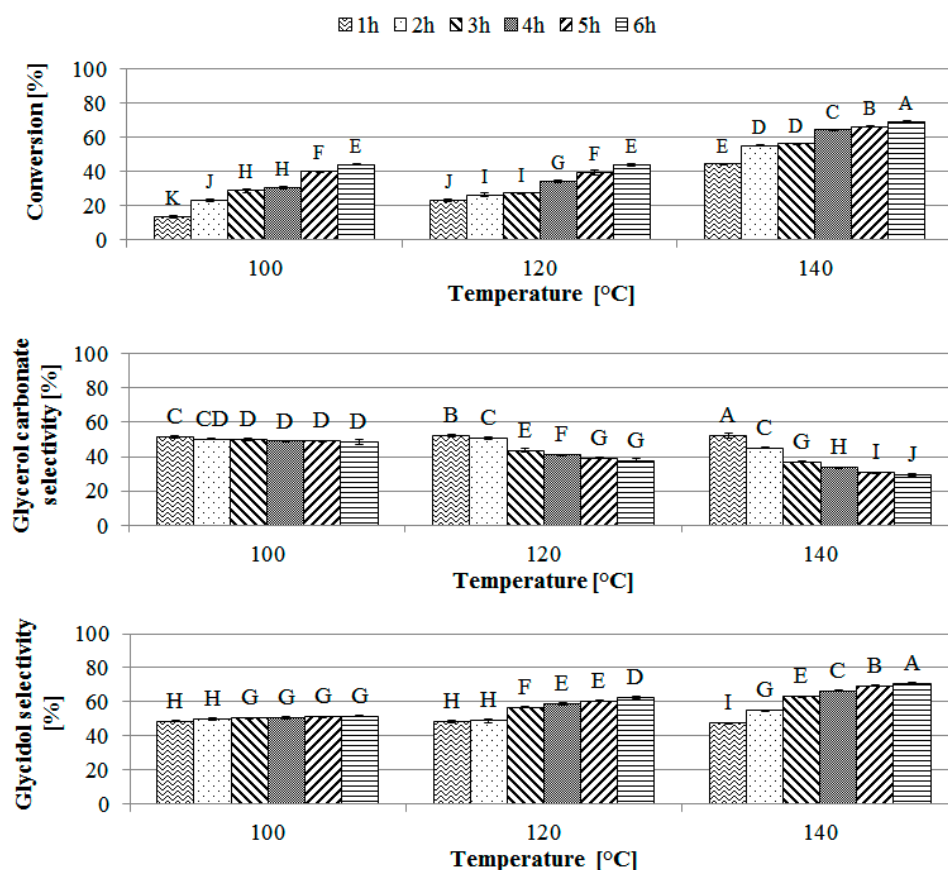


Figure 5. The influence of temperature on the catalytic performance of a biosolids-based catalyst. Reactions were carried out using a catalyst:glycerol ratio of 9% (wt/wt), a 2:1 molar ratio of urea:glycerol, and an air stream. The conversion and selectivity at three different temperatures were examined: 100 °C, 120 °C, and 140 °C. The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95%).

According to ANOVA outputs, parameters investigated (reaction time and temperature) were statistically significant for conversion values during urea glycerolysis ($p < 0.05$), and for selectivity only for temperature values below 100 °C. *t*-tests showed the statistical similarity for the selectivity averages at 100 °C. The catalytic system at 100 °C was not totally selective at any reaction time tested, leading to the formation of an equal amount of glycerol carbonate and glycidol. At 120 °C, moving from 1 h to 6 h increased the selectivity for glycidol from $48.2 \pm 0.4\%$ to $62.7 \pm 0.9\%$. This trend was clearer at 140 °C with an increase in selectivity from $46.2 \pm 0.2\%$ after 1 h to $70.2 \pm 0.4\%$ after 6 h. Decarboxylation of glycerol carbonate to glycidol is due to the synergistic effect of acidic-basic functionalities on the surface of the catalysts and the radical-rich reaction environment promoted by urea splitting [11]. The contribution of urea splitting was magnified as the temperature was increased to 140 °C, becoming the predominant driving force of the process.

2.4. Influence of the Molar Ratio of Urea/Glycerol

The effect of urea/glycerol ratio was also investigated at 140 °C using a catalyst loading of 9 wt % and an air stream to facilitate the removal of NH_3 formed during the reaction (Figure 6). Decreasing the molar ratio of urea/glycerol from 2:1 to 1:1 led to a significant ($p < 0.05$) decrease in conversion values for each time tested, with a maximum conversion of $59.9 \pm 1.2\%$ achieved after 6 h. In addition,

a urea/glycerol molar ratio of 1:1 led to a decrease in the maximum glycidol production (down to $65.7 \pm 0.9\%$ after 6 h), caused by the decreased amount of radical species in the reaction environment. Based on ANOVA outputs, parameters investigated (reaction time and urea/glycerol) were statistically significant for conversion during urea glycerolysis ($p < 0.05$). These results support the hypothesis that the radical heterolytic splitting of urea played a major role in the process at reaction temperatures greater than $140\text{ }^{\circ}\text{C}$, promoting the radical reaction pathway, instead of the non-radical one.

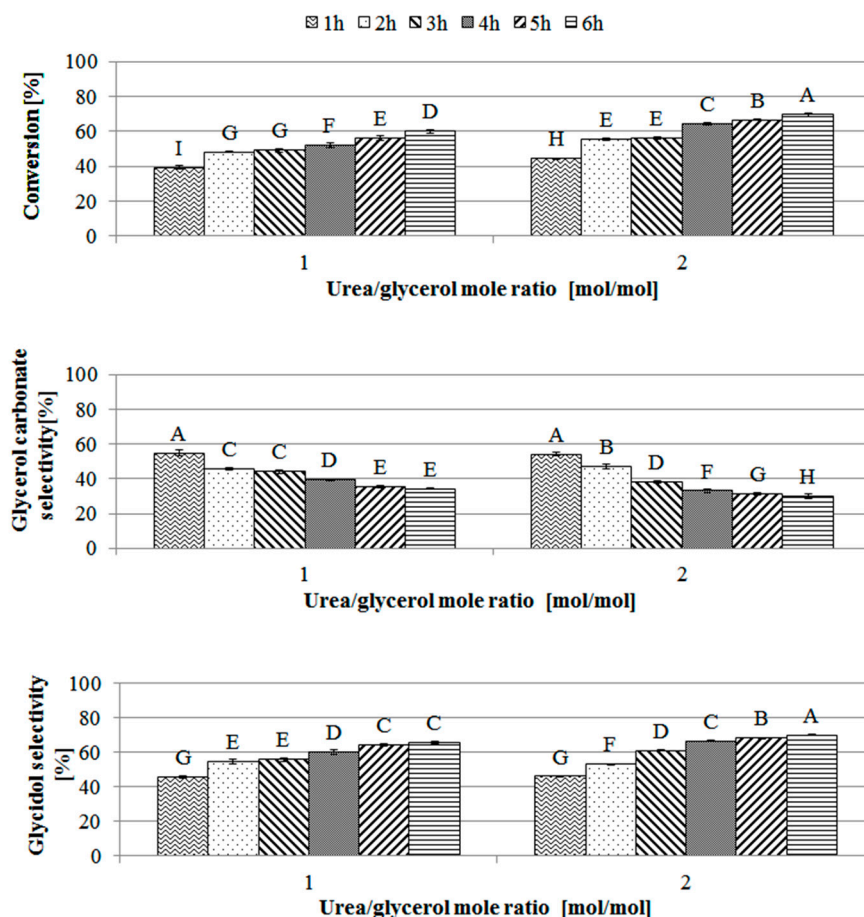


Figure 6. The influence of molar ratio on the catalytic performance of a biosolids-based catalyst. For the reactions shown below, the catalyst:glycerol ratio was maintained at 9 wt % at a reaction temperature of $140\text{ }^{\circ}\text{C}$ and using an air stream. To determine the effect of using different urea:glycerol ratios, two molar ratios were employed: 2:1 and 1:1 (mol/mol). The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95%).

2.5. Influence of Residual Atmosphere

Formation of NH_3 as a byproduct during urea alcoholysis is a considerable issue in terms of both the reaction kinetics and the sustainability of the process. In order to remove NH_3 from the reaction environment, urea glycerolysis could be carried out using reactive distillation procedures [35], reduced pressure [32], or using a stream of air. In order to remove NH_3 , three different gas streams (air, N_2 , CO_2) were evaluated at $140\text{ }^{\circ}\text{C}$ using a catalyst loading of 9 wt % and a 2:1 molar ratio of urea:glycerol (Figure 7).

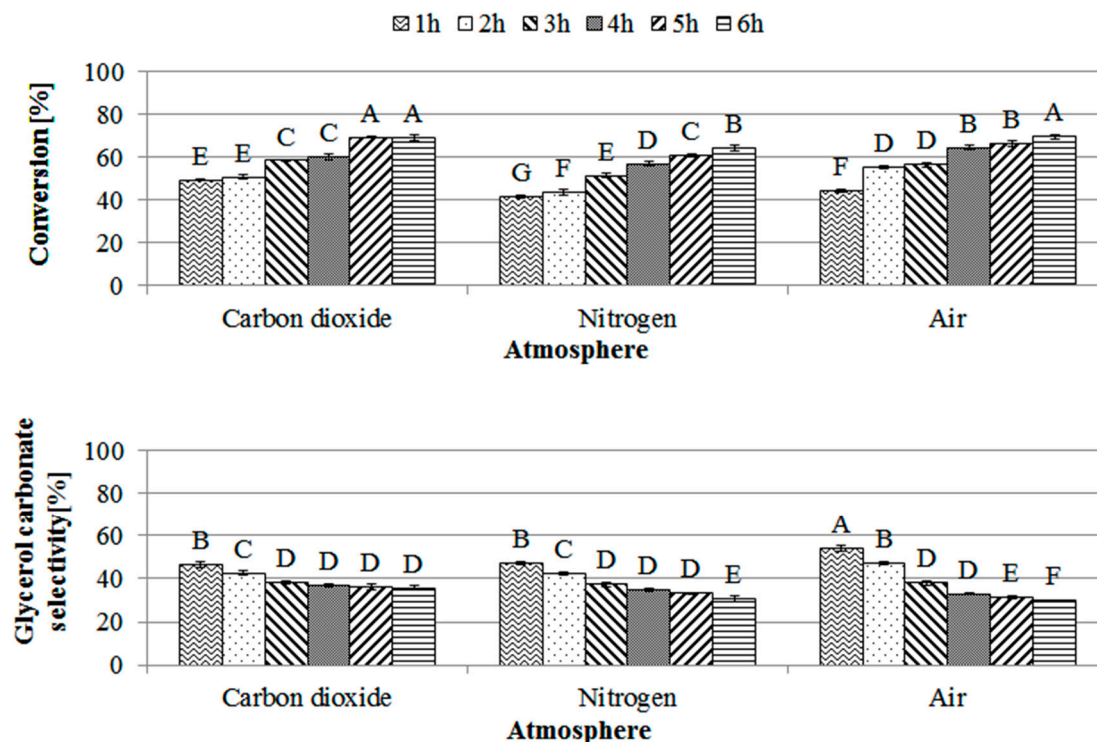


Figure 7. The influence of atmosphere on the catalytic performance of a biosolids-based catalyst. The following reaction conditions were used: A catalyst:glycerol ratio of 9 wt %, a temperature of 140 °C, a 2:1 molar ratio of urea:glycerol, and three different gas streams to remove NH_3 formed during the reaction (air, N_2 , CO_2). The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95%).

According to ANOVA, parameters investigated (reaction time and residual atmosphere) were both statistically significant and relevant for conversion values during urea glycerolysis, assuming $p < 0.05$, but their influence on selectivity values was smaller. Adopting a N_2 stream in place of the air stream that was used in the experiments described above did not result in a significant difference in the maximum conversion after 6 h. For the N_2 stream, a significant ($p < 0.05$) increase in conversion values was observed as the reaction time was lengthened from 1 h to 5 h, but no further increase was observed when the reaction time was increased to 6 h. Using CO_2 , the conversions were generally lower with a maximum conversion of $64.0 \pm 1.2\%$ achieved after 6 h, which was significantly lower than the values achieved using air or N_2 for an equivalent reaction time. Furthermore, the selectivity of glycidol was lower ($35.8 \pm 1.2\%$) when CO_2 was used as the atmospheric gas, likely because the increase in CO_2 partial pressure decreased the rate of decarboxylation of glycerol carbonate. Based on the results shown, the use of an air stream for the removal of NH_3 is likely preferred given that it had the highest conversion rate and glycidol selectivity, and is also the cheapest option.

2.6. Influence of Recycling on Urea Glycerolysis on the Conversion Rate

Next, we examined whether or not the biosolids-based catalyst could be recycled. The activity of the catalyst was monitored after each of four runs, with each reaction conducted at 140 °C for 6 h using a catalyst loading of 9 wt %, a 2:1 molar ratio of urea:glycerol, and a stream of air to remove NH_3 formed during the reaction (Figure 8). The activity of the biosolids-based catalyst decreased from $69.4 \pm 0.9\%$ for the first run to $56.4 \pm 1.3\%$ for the fourth run. Similarly, the glycidol selectivity dropped from $71.1 \pm 0.7\%$ to $65.6 \pm 0.9\%$. The decreased catalyst activity was likely attributable to

the leaching of metals (Table 1), caused by the formation of soluble metal species as a consequence of reactions between urea-derived radicals and metal surface sites. In addition, chemical modification of the organic fraction of the biosolids-based material was observed through ATR-FTIR analysis of the recycled catalyst recovered after the fourth catalytic run (Figure 2). The chemical modifications could be ascribed to the formation of amino and amido groups (IR bands of $\nu_{\text{-NH}}$ in the range of $3500\text{--}3400\text{ cm}^{-1}$ and amido $\nu_{\text{-C=O}}$ in the range of $1800\text{--}1700\text{ cm}^{-1}$) caused by the reaction between the urea-derived radical species and the aromatic organic matrix.

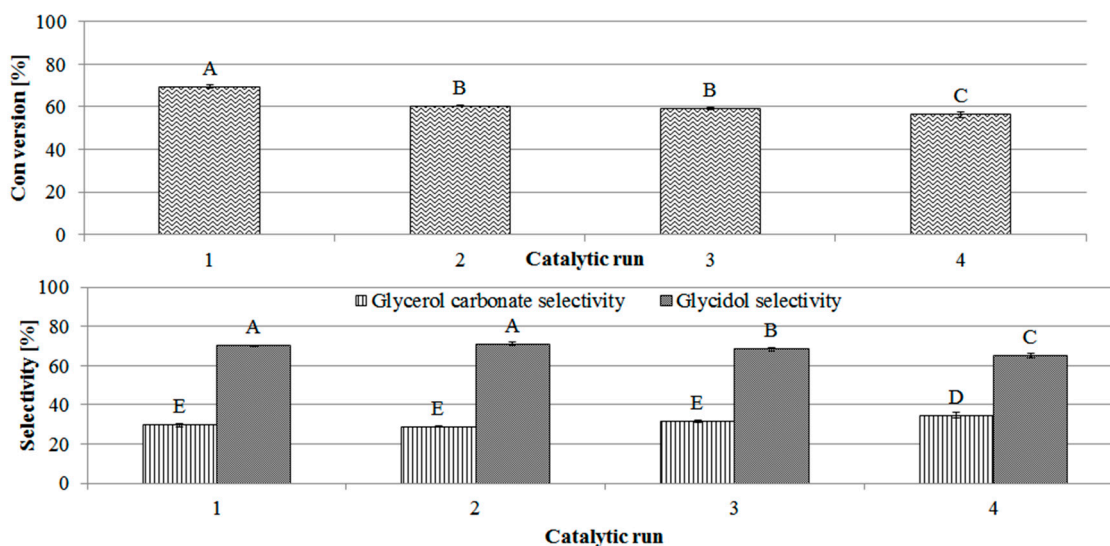


Figure 8. Recyclability of the biosolids-based catalyst. during four catalytic runs (catalyst/glycerol 9 wt %, 140 °C, urea/glycerol 2 mol/mol, air stream, 6 h) The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95%).

2.7. Comparison between Biosolids Based Catalysts and Heterogenous Catalysts

Several materials were studied as catalysts for urea glycerolysis. Among them, zinc-based catalysts play a major role. As reported by several authors [12,36–38], use of different zinc salts induced different conversion and glycerol carbonate selectivity during urea glycerolysis. Zinc-halogen binary salts showed a close relationship between anions and zinc activity with an increase in conversion from 64.3% using ZnF_2 to 81.4% using ZnBr_2 at 150 °C for 4 h. The increased mobility of bromine with respect to fluorine also affected glycerol carbonate selectivity with an increase from 84.1% to 97.2% [36]. Our biosolids-based catalyst is out-performed by zinc salts but it is active ZnO that likely promotes a conversion of 69.9% at higher temperature (150 °C for 4 h) with an inferior selectivity for glycerol carbonate (68.5%). Furthermore, our biosolids-based catalyst is comparable with cobalt nanoparticles supported on ZnO [37], and zinc-tin catalysts [38] that reached conversion around 69% at 150 °C. Other expensive catalysts such as Au and Pd nanoparticles [39], ionic liquids [40] or lanthanum oxides [41] could be used achieving conversion up to 84% and selectivity around 87%, but they require several steps for preparation and high control of reaction conditions. Nevertheless, a key advantage to our biosolids-based catalyst is the fact that it can be generated from a negative-value waste stream using a thermal treatment that has also been shown to drastically improve settling rates [31]. Therefore, thermal hydrolysis of biosolids may simultaneously address a growing problem in the treatment of municipal wastewater, while at the same time generating a value-added heterogeneous catalyst.

3. Materials and Methods

3.1. Materials

Tetrahydrofuran (HPLC grade, >99.9% without stabilizers), methanol (HPLC grade, >99.9%), urea (98%), NaOH (>99%), HCl (37%) and methyl nonadecanoate (used as internal standard for gas chromatography) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glycerol (98%) and heptane (>99%) were purchased from Fisher Chemical (Fair Lawn, NJ, USA). Gases (Air, CO₂, N₂, H₂, He) were purchased from Praxair Inc. (Edmonton, AB, Canada).

3.2. Methods

3.2.1. Catalytic Acetylation of Glycerol

10 g of glycerol were put into a single-neck round-bottom flask with urea (urea/glycerol molar ratio (mol/mol) of 2 or 1), the biosolids based catalyst (catalyst/glycerol weight ratio (wt/wt) of 12%, 9%, 6%, 3%, 0%), which was then connected to a condenser. The reaction mixtures were stirred and heated at different temperatures (100 °C, 120 °C, 140 °C) for 6 h with sampling every hour. During the reaction, a stream of air, N₂, or CO₂ was employed to remove NH₃ formed during the process. After 6 h, the reaction mixtures were cooled at room temperature and the catalyst was recovered through centrifugation (7155 × *g* for 10 min), washed with acetone three times (5 mL for each wash), dried overnight at 105 °C, and then analyzed. Each test was replicated three times.

3.2.2. Gas Chromatography and Mass Spectrometry

100 µL of the crude reaction mixture were diluted with 0.5 mL of tetrahydrofuran and 0.5 mL of methanol, with 10 mg of methyl nonadecanoate added as internal standard. The solution was analyzed using a gas chromatograph (6890N; Agilent Technologies, Fort Worth, TX, USA) equipped with an autosampler (Agilent 7683 series; Agilent Technologies, Fort Worth, TX, USA), a flame ionization detector, and a mass spectrometer (Agilent 5975B inert XL EI/CI MSD; Agilent Technologies, Fort Worth, TX, USA). Analyses were carried out by injecting 1 µL of the samples onto a DB-5 column (100 m × 250 µm × 0.25 µm; Agilent Technologies, Fort Worth, TX, USA) using the gas chromatographic method described above [42]. The concentration of unreacted glycerol was evaluated using a five-point calibration curve ($m = 0.185 \pm 0.02$, $R^2 = 0.994$) obtained using methyl nonadecanoate as the internal standard.

3.2.3. Characterization of Inorganic Content in the Biosolids-Based Catalyst

The amount of inorganic residue contained in the solid material recovered after thermal hydrolysis of biosolids at 280 °C for 1 h was determined through incineration of 5 g of the sample at 450 °C for 6 h using a 48000 Furnace (Barnstead Thermolyne, Dubuque, IA, USA) in accordance with the method developed by Benitez et al. [43]. This test was repeated three times. Compositional analysis of the inorganic content was performed using a Thermo iCAP 6000 series Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Thermo Fisher Scientific, Madison, WI, USA) at the Natural Resources Analytical Laboratory (Department of Renewable Resources, University of Alberta).

3.2.4. Quantification of Total Surface Acidic Groups

The total surface acidic groups present in the biosolids-based catalyst were determined through titration based on the procedure proposed by Boehm [44]. Briefly, 150 mg of catalyst were put in a plastic tube with 50 mL of 0.05 N NaOH and stirred at room temperature for 24 h. Afterwards, the mixture was centrifuged at 7155 × *g* for 10 min and the solid was removed. 25 mL of centrifuged solution were then neutralized with a standard solution of 0.05 N HCl. The total surface acidic groups were determined as the difference between the mmol of NaOH 0.05 N before and after the titration, which is equivalent to the mmol of 0.05 N HCl added.

3.2.5. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) analyses were carried out using a Nicolet iS50 (Thermo Fisher Scientific, Madison, WI, USA) in the range of 4000–600 cm^{-1} with a band of resolution of 2 cm^{-1} . These analyses were performed at the nanoFAB Centre at the University of Alberta.

3.2.6. Statistical Analysis

One-way and Two-way ANOVA tests with a significance level of 0.05 ($p < 0.05$) were carried out using Excel™ software (Microsoft Corp., Redmond, WA, USA) and the “Data analysis” plug-in.

4. Conclusions

The solid recovered after hydrolysis of biosolids at 280 °C for 1 h has been successfully employed as a catalyst for urea glycerolysis. It showed a remarkably activity reaching a maximal conversion value of $70.1 \pm 0.5\%$ and a glycidol selectivity of up to $70.8 \pm 0.9\%$. Temperature had the greatest impact on the conversion and selectivity, and was likely caused by the elevated heterolytic radical splitting of urea that drastically enhanced the reaction efficiency as the temperature was increased. For the same reason, increasing the molar ratio of urea:glycerol to 2:1 showed better performance compared with values obtained using a ratio of 1:1. Increasing catalyst loading slightly improved the conversion, but did not strongly affected the selectivity. Furthermore, the use of an air or N_2 stream to remove NH_3 formed during the process was shown to more effective than the use of CO_2 . The catalyst could be recycled, but a decreased catalytic activity was observed after the fourth catalytic run, though conversion rates were still reasonably high. In future studies, a continuous process (distillation of products and supplemental addition of reagents) will be studied to improve the life of the catalyst. In conclusion, we have proven that the biosolid-based material functions as a reliable catalyst for production of glycidol through a urea glycerolysis reaction, providing potential benefits to both the biodiesel industry and wastewater management facilities.

Author Contributions: Conceptualization, M.B. and D.C.B.; Methodology, M.B.; Formal Analysis, M.B.; Investigation, M.B. and C.Z.; Data Curation, M.B.; Writing-Original Draft Preparation, M.B.; Writing-Review & Editing, M.C. and D.C.B.; Supervision, D.C.B.; Project Administration, M.C. and D.C.B.; Funding Acquisition, M.C. and D.C.B.

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